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Continuum lumping modelling for step growth polymerisation mechanism

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ABSTRACT

Polymerisation occurs by chain addition or step-growth mechanisms. The yield and the concentration distribution of monomers, dimers, trimers and higher order polymers can depend on the molecular weight or some other variable which can be unequivocally linked to any given compound. Continuum lumping is a methodology widely used to describe the kinetic and thermodynamic behaviour of complex reactive mixtures of diverse components all undergoing similar types of reactions (e.g., cracking, pyrolysis, oligomerisation). The methodology is particularly convenient when the number of species involved is very large and the species can be characterised by properties which are measured in a continuous fashion, as for instance in a chromatogram. By applying the lumping methodology, a large reactive system can be reduced to a simpler and more tractable one. A model, based on the continuum lumping approach, is proposed to predict the molecular weight distribution of polymers during polymerisation. The main aim of this work is to assess the suitability of the application of the continuum lumping approach to polymerisation. The results obtained from a continuous model are assessed, at this stage, only qualitatively; nevertheless, by analysing the weight distribution and the average of such distribution, conclusions can be reached to assess the predictive capability of the lumping methodology. The model is tested for two selected case studies and the product distribution is obtained at various times.

Keywords: Continuum lumping; Modelling; Polymerisation

1. Introduction

Multi-component complex reactive systems are very common in industrial processes, spanning from hydrocracking to polymerisation, from air pollution to pyrolysis, to cite just a few examples. Those are systems where the individual components of the mixture are numerous and it is difficult to identify them in detail. The reduction of the dimensionality of the system having a large number of components furnishes systems constituted by a lower number of components. As an example, one could imagine of substituting a subset of similar components, such as stereoisomers, with a single component, or "lump" having the properties of the underlying sub-mixture. In addition, when one is not interested in the fine-grained structure of the system, but only in some gross *overall* properties (e.g., the total concentration of all species of a certain type) the "overall lumping approach" can be performed. It is important to note that the overall description can be attempted both in a discrete and continuous fashion; however, if the number of components is very large, it is more convenient to attempt a continuous description. The term "overall" corresponds in projecting the space of N components into a sub-space having *one* dimension (namely $N\hat{}=1$). In addition, it is customary to call "lumping" the average of a mixture over the composition space, even if the origin of the term and its development have often followed various routes as discussed by Wei (1991). The "*continuum lumping*" is shown to be convenient when a large number of species exists and the species are measured in a continuous fashion, as, for instance, with a chromatogram or boiling point curve. In this case, an index, x, is introduced; $A(x)dx$ represents a property of the sub-mixture whose index lies in $(x, x+dx)$.

Step growth polymerisation involves the reaction between the functional groups of any molecule in the reaction mixture; consequently, by repeated reaction, long chains are gradually produced. Parameters such as molecular weight

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